Determination of nitrogen exchange between Lake Balaton and the atmosphere

PhD theses

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Introduction

The nutrient load of freshwater ecosystems derives basically from different water sources and atmospheric input. Nutrient enrichment causes eutrophication processes. The word „eutrophic" means rich in nutrients, namely the eutrophication means that the water body gets access influx from the natural and anthropogenic sources.

Eutrophication that also occurs as a natural aging process of lakes came in the center of public interest in the 1960-ies in countries with developed industry and agriculture. The phenomenon was observed as the consequence of increased external load of nitrogen and phosphorus as the two most important plant nutrients.

The sources of the nitrogen and phosphorus enrichment can be the load from the catchment area (communal and industrial wastewater), nutrients washed off by the surface and subsurface runoff from the agricultural and urban areas, furthermore the atmospheric load onto the water surface and catchment area. For Hungarian and Eastern European lakes generally the only limiting nutrient is the phosphorus, more precisely the so called biological available phosphorus.

According to the nutrient balance determined by *Jolánkai* és *Bíró* (2005) generally the phosphorus load is one order of magnitude lower than that of nitrogen. The optimum N/P ratio is 16:1 for the nitrogen, 10:1, than nitrogen shortage, if it changes to 20:1 than phosphorus shortage exists in the ecological system. In the nutrient balance determined by *Jolánkai* and *Bíró* (2005) the atmospheric load was taken into account as a rough estimate, therefore in this work we aimed to estimate a more accurate balance including more components.

Objectives

The objective of my research is to determine the nitrogen balance between the atmosphere and Lake Balaton. Besides the estimation of the effect of the depositing components, emission processes are also examined to calculate the net fluxes.

The dry and wet deposition of nitrogen containing gases and aerosol particles and in case of ammonia gas the net flux must be considered for the determination of the total N-load. The exchange rate of nitrogen between the atmosphere and Lake Balaton was determined for the period between 2001 and 2004 on the basis of a detailed measurement program.

Methods

Among the balance components I determined the ammonia exchange by the compensation-point model for the period between 2001 and 2004. Using the compensation-point model the observed trace gas fluxes have been calculated from the difference of the measured atmospheric concentrations above the water surface (at height z) and the compensation-point concentration at the roughness height (z_0) and using the dry deposition velocity. The atmospheric concentration was partly measured on site, partly was interpolated from data of background monitoring stations. The compensation-point concentration (equilibrium concentration above water) was derived from the physical and chemical parameters of the water. The deposition velocity is determined as reciprocal value of sum of resistances to deposition, namely the aerodynamic resistance (R_a), the boundary layer resistance (R_b) and the surface resistance (R_c). The surface resistance of ammonia and nitric acid above water can be neglected.

For the compensation-point model the turbulent fluxes were calculated by the resistance model based on the Monin–Obukhov similarity-theory. Beside that I also applied the so-called FLake lake model, which is able to determine the temperature profile of shallow lakes and the surface energy budget components. The model based on the Monin–Obukhov similarity theory uses the parameterization of *Businger et al*. (1971) for the determination of the universal functions, while the FLake model uses the parameterization of *Dyer* (1974). Knowing the universal functions I have calculated the different resistance terms.

The calculation of the compensation-point concentration besides the water temperature requires the pH and the ammonia + ammonium concentration in the water. For my calculations I have used the average concentrations of bi-weekly samples collected at 4 monitoring stations around Lake Balaton.

Using each input parameter of the compensation-point model I have calculated the ammonia flux between 2001 and 2004. The model was programmed in Fortran language.

The ammonia compensation-point concentration was calculated by two different methods, firstly using the classical *Henry*-law, and secondly by *Hales–Drewes* solubility theory where I considered the effect of dissolved CO_2 on the solubility of ammonia.

The above mentioned model was also used for the determination of the nitric acid deposition. In this model the only difference from the ammonia compensation-point model is that the compensation-point of nitric acid is zero since at the slightly basic pH of the water no

nitric acid is released from the water into the air, i.e. in this pH range the dissociation of the nitric acid is complete, HNO_3 molecules do not exist in the water. For this reason the direction of the nitric acid flux can only be from the atmosphere to the water (deposition).

The compensation-point model was validated by the gradient method in case of ammonia and nitric acid, based on a summer measurement campaign between 12 and 25 July 2002. For the determination of the gradient fluxes the atmospheric ammonia and nitric acid concentration was measured at 2 different heights. The flux rate was calculated based on the concentration gradient and the turbulent diffusion coefficient of the sensible heat flux calculated from micrometeorological measurements.

Since in case of aerosol particles only deposition exists I used a simpler, than for gases deposition model for the determination of dry deposition. Moreover, in contrary to the gases, the deposition of aerosol particles depends less on the characteristics of the surfaces. However, the deposition velocity of particles strongly depends on their size distribution.

The deposition of a certain size of aerosol particles is derived from the product of the deposition velocity of the particle and their concentration in that range. In order to determine the mean deposition flux of the particles the size distribution, the mean deposition velocity of a certain size fraction and the concentration in the given size fraction must be known. The concentration values were considered partly from measurements on site measurement data, partly from interpolated data similarly to that of the gases. Theoretically, the integral for the whole size distribution of the aerosol particles is used for calculation of dry deposition, however in my work I used an average size of the particles that is derived from size distribution curves. I estimated an average dry deposition velocity from the literature data for the given mean size.

The wet deposition of N-compounds was determined from the chemical composition of precipitation and the precipitation data. The rate of the wet deposition was calculated as the product of the concentration of the nitrate and ammonium ion in the precipitation and the precipitation amount.

Results, conclusions

1. According to my investigation on the nitrogen exchange between Lake Balaton and the atmosphere I found that the average total nitrogen load to the lake is 440 t N $year^{-1}$ between 2001 and 2004. Seeing that the Hungarian background pollution has not been changed considerably since then, this value could also be representative nowadays.

2. Primarily the wet deposition dominates in the nitrogen load, resulting in share of 96% in the total flux in contrary to the surfaces covered by low and high vegetation, where the dry deposition rate is generally higher than that of wet deposition. The main reason of this phenomenon is the difference in the surface characteristics (roughness) of water and terrestrial surfaces. For this reason the dry deposition of either the gases or the ammonium and nitrate particles is not considerable.

3. I compared the monthly evaporation values calculated with the Meyer formula (the method is used at the Hungarian Meteorological Service for the determination of the evaporation) with the results of FLake and resistance models. After the comparison, the correlation of the evaporation between the Meyer formula and FLake model is $r = 0.93$, and with the resistance model is $r = 0.80$. The results show a significant correlation at probability level of $p = 0.01$. I considered that the usage of the more complicated FLake model at certain conditions is not necessary; the usage of the more simple resistance model gives results accurate enough.

4. The pH of Lake Balaton ranges between 8.3 and 8.9 where both dissolved ammonia and also ammonium exist together. It allows both the deposition of ammonia and the emission from the lake as well. Since the compensation-point concentrations determined by the chemical and physical conditions in the lake were both lower and higher than the actual atmospheric concentration the ammonia flux had bi-directional fluxes during my investigations. The ammonia net flux averaged for the 4 years is 32.7 t N $year^{-1}$ emission, showing a not negligible but not dominant contribution in the nitrogen balance. The nitric acid flux is −21.8 t N $year^{-1}$ (deposition).

5. Since the ammonia net flux mainly depends on the NH_3 and NH_4^+ content in the water and ammonia concentration in the air, in case of a high N-load into the lake the compensation-point concentration is increasing resulting in higher ammonia emission. It means a negative feedback mechanism exists, which can buffer the effect of the nitrogen load. In the lack of sufficient nitrogen since the low NH_3 and NH_4^+ content in the water the compensation-point concentration decreases, which results in the change of the direction of the flux, so the lake absorbs the necessary nitrogen from the air. Partly the consequence of this phenomenon is that eutrophication of Lake Balaton is phosphorus limited.

6. The compensation-point model was validated by the gradient method, based on a summer measurement campaign between 12 and 25 July 2002. For this period the fluxes were determined and compared by models and measurements as well. In case of ammonia the correlation was found to be $r = 0.72$ when the effect of CO_2 was considered (see thesis 7th), correlation is significant at probability level of $p = 0.01$. For nitric acid the correlation was $r = 0.68$, at the same level.

7. The dissolved carbon dioxide in the water probably affects the solubility of ammonia. According to previous investigations the solubility of ammonia decreases (volatility increases) in presence of CO_2, which was refused by some latter research. According to my results no significant correlation was found between the gradient measurements and compensation-point model based on single Henry's law and the values were different by one order of magnitude. In contrast with the theory of Hales–Drewes taking into account the effect of carbon dioxide, which gives significant correlation and the modeled and measured average values are also the same. According to my calculations the effect of CO_2 depends on the pH, below $pH = 8.25$ carbon dioxide reduces, above that increases the solubility of ammonia. I suppose it is the consequence of the fact that at lower pH the volatile carbamic acid (formed by the reaction of dissolved ammonia and carbon dioxide) helps ammonia to be emitted into the atmosphere. At higher pH carbamic acid dissociates into ions keeping ammonia in solution (lowers the volatility).

References:

Businger, J.A., Wyngaard, J.C., Izumi, Y., Bradley, E.F. (1971): Flux-Profile Relationships in the Atmospheric Surface Layer. *Journal of Atmospheric Sciences* **28**: 181–189.

Jolánkai G., Bíró I. (2005): *A Balaton tápanyag terhelésének mérlege, mérése és modellezése, 2004.* A munka második részének zárójelentése. Témaszám: 714/31/648601. VITUKI Kht. Vízminőség-védelmi Szakágazat. 77p.

Dyer, A.J. (1974): A review of flux-profile relationships. *Boundary-Layer Meteorology* **7**: 363–372.

Publications related to the dissertation:

Kugler, Sz., Horváth, L. (2004): Estimation of the nitrogen loading from the atmospheric dry deposition of ammonium and nitrate aerosol particles to Lake Balaton. *Időjárás,* Vol. 108. No. 3. pp. 155–162.

Kugler, Sz., Horváth, L., Mészáros, R., Weidinger, T., Gyöngyösi, A.Z. (2004): Measuring and modeling of ammonia and nitric acid exchange between the atmosphere and Lake Balaton. *Geophysical Research Abstract*, Vol. 6. CD-ROM. EGU04-A-05587.

Kugler, Sz., Horváth, L., Lewandowska, A. (2007): Measurement and modelling of the exchange of ammonia gas between atmosphere and aquatic ecosystems. Seventh Annual Meeting of the European Meteorological Society; Eight European Conference on Applications of Meteorology *(ECAM) Abstracts*, Vol. 4, EMS2007-A-00255

Kugler Sz., Horváth L. (2008): A nitrogénvegyületek kicserélődésének vizsgálata a Balaton és a légkör között. *OTKA szakmai zárójelentés* (A nitrogénvegyületek kicserélődésének vizsgálata a Balaton és a légkör között, T-46824), Budapest. 14p.

Kugler, Sz., Horváth, L., Machon, A. (2008): Estimation of nitrogen balance between the atmosphere and Lake Balaton and a semi natural grassland in Hungary. *Environmental Pollution* 154 pp. 498–503.

Kugler Sz., Horváth L., Weidinger T. (2008): Az ammónia kicserélődése a légkör és vízi ökológiai rendszerek között. In: (ed.: Sáhó Á.) A levegőkörnyezet állapota: ökológiai kölcsönhatások és egészségügyi kockázatok. *A 33. Meteorológiai Tudományos Napok 2007 kiadványa*, www.met.hu/pages/seminars/metnapok/33_MTN_2007.pdf , pp. 54-57.

Horvath, L., Weidinger, T., Machon, A., Tuba, Z., Nagy, Z., Grosz, B., Führer, E., **Kugler, Sz**., Pogány, A., Huszár, H. (2011): National contributions to the assessment of nitrogen, 8.8 Hungary. *COST729 Assessing and managing nitrogen fluxes in the atmosphere-biosphere system in Europe, Final Report* (*Edited by Bleeker A. and Erisman, J.W.*) *Wageningen Academic Publishers,* 130–138.

Kugler, Sz., Horváth, L. Weidinger, T. (2013): Measurement and modelling of the exchange of ammonia gas between atmosphere and Lake Balaton. Thirteenth Annual Meeting of the European Meteorological Society; Eleventh European Conference on Applications of Meteorology *(ECAM) Abstracts*, Vol. 10, EMS2013-495.

Kugler, Sz., Horváth, L., Weidinger, T. (2014): Modeling dry flux of ammonia and nitric acid between the atmosphere and Lake Balaton. *Időjárás*. Vol. 118. No. 2. pp. 93–118 (In press).